

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-289178

(43)Date of publication of application : 04.10.2002

(51)Int.Cl. H01M 4/02

H01M 4/04

H01M 4/38

H01M 4/66

H01M 10/40

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(54) LITHIUM SECONDARY BATTERY AND ELECTRODE FOR IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery electrode of high discharge capacity and charge/discharge cycle characteristics wherein an active material layer comprising a metal which alloys with Li is provided on a collector layer comprising a metal which does not alloy with Li.

SOLUTION: On a surface on the side opposite to the collector layer of the active material layer, a surface coat layer comprising a metal which does not alloy with Li or that comprising an alloy of a metal which does not alloy with Li and a metal which alloys with Li is provided.

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CLAIMS

[Claim(s)]

[Claim 1]In an electrode for lithium secondary batteries by which an active material layer which consists of Li and metal to alloy was provided on a collector layer which consists of Li and metal which is not alloyed, An electrode for lithium secondary batteries, wherein a surface coated layer which consists of an alloy of a surface coated layer or Li which consists of Li and metal which is not alloyed, metal which is not alloyed, Li, and metal to alloy is provided on said collector layer of said active material layer, and a field of an opposite hand.

[Claim 2]The electrode for lithium secondary batteries according to claim 1 being the same metal as Li of said surface coated layer, and metal which metal to alloy alloys with Li of said active material layer.

[Claim 3]The electrode for lithium secondary batteries according to claim 1 or 2 being the same metal as Li of said surface coated layer, and metal which metal which is not alloyed does not alloy with Li of said collector layer.

[Claim 4]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-3, wherein Li and metal to alloy are Sn.

[Claim 5]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-4, wherein Li and metal which is not alloyed are Cu(s).

[Claim 6]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-5, wherein said active material layer is formed by depositing Li and metal to alloy on a substrate used as said collector layer.

[Claim 7]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-5, wherein said collector layer is formed by depositing Li and metal which is not alloyed on a substrate used as said active material layer.

[Claim 8]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-7, wherein said surface coated layer is formed of the plating method or sputtering process on said active material layer.

[Claim 9]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-8, wherein said surface coated layer consists of Cu(s).

[Claim 10]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-9, wherein said surface coated layer consists of an Sn-Cu alloy.

[Claim 11]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-10, wherein a compound phase which an ingredient of said surface coated layer and an ingredient of said active material layer mixed to an interface of said surface coated layer and said active material layer is formed.

[Claim 12]The electrode for lithium secondary batteries according to claim 11, wherein said compound phase is formed by heat treatment after said surface coated layer formation.

[Claim 13]An electrode for lithium secondary batteries given in any 1 paragraph of claims 1-12, wherein thickness of said surface coated layer is 0.2 micrometer or less.

[Claim 14]A lithium secondary battery comprising:

A negative electrode which becomes any 1 paragraph of claims 1-13 from an electrode of a statement.

An anode.

Nonaqueous electrolyte.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the lithium secondary battery which used the electrode for lithium secondary batteries, and this.

[0002]

[Description of the Prior Art]In recent years, battery characteristics, such as charge and discharge voltage, charge-and-discharge cycle life property, and a conservation characteristic, are greatly influenced by the electrode for which the lithium secondary battery with which research and development are done briskly is used. From this, improvement in a battery characteristic is achieved by improving an electrode active material.

[0003]When the lithium metal was used as negative electrode active material, per weight and per volume could constitute the cell of the high energy density, but lithium deposited in the shape of a dendrite at the time of charge, and there was a problem of causing an internal short circuit.

[0004]On the other hand, the lithium secondary battery using lithium, aluminum, silicon, tin to alloy, etc. as an electrode is electrochemically reported in the case of charge

(SolidState Ionics, 113-115, p57 (1998)).

[0005]

[Problem(s) to be Solved by the Invention]These people have found out that the electrode which deposited thin films, such as tin alloyed with lithium by the electrolysis plating method etc., on charge collectors, such as copper foil, as an electrode for lithium secondary batteries has large service capacity, and shows a comparatively good cycle characteristic.

[0006]However, in order to consider it as the practical electrode for lithium secondary batteries, it is required to improve a cycle characteristic further. The purpose of this invention has large service capacity, and there is in providing the lithium secondary battery using the electrode for lithium secondary batteries and this excellent in the charge-discharge cycle characteristic.

[0007]

[Means for Solving the Problem]This invention on a collector layer which consists of Li (lithium) and metal which is not alloyed, It is the electrode for lithium secondary batteries in which an active material layer which consists of Li and metal to alloy was provided, It is characterized by providing a surface coated layer which consists of an alloy of a surface coated layer or Li which consists of Li and metal which is not alloyed, metal which is not alloyed, Li, and metal to alloy on a collector layer of an active material layer, and a field of an opposite hand.

[0008]In this invention, since a surface coated layer containing Li and metal which is not alloyed is provided on an active material layer, a reaction of the surface of an active material layer and an electrolysis solution can be inhibited by this surface coated layer. As a result, degradation of the active material layer surface can be controlled and a charge-discharge cycle characteristic can be raised.

[0009]In this invention, metal which forms Li, a solid solution, or an intermetallic compound is mentioned as Li and metal to alloy. As such metal, Sn (tin), germanium (germanium), aluminum (aluminum), In (indium), Mg (magnesium), Pb (lead), Bi (bismuth), Zn (zinc), etc. are mentioned. As for Li and metal to alloy, two or more sorts may be contained. Therefore, into an active material layer, two or more sorts, Li and metal to alloy, may be contained, and it may be formed from an alloy of Li and two or more sorts of metal to alloy.

[0010]In this invention, metal which does not form Li, a solid solution, or an intermetallic compound is mentioned as Li and metal which is not alloyed. Specifically, metal in which an alloy state does not exist in a binary-condition figure with Li is mentioned. As Li and metal which is not alloyed, Cu (copper), Fe (iron), nickel (nickel), Co (cobalt), Mn (manganese), Ti (titanium), Zr (zirconium), Mo (molybdenum), W (tungsten), Ta (tantalum), etc. are mentioned, for example. Li and two or more sorts of metal which is not alloyed may be contained.

[0011]In this invention, a surface coated layer may be formed from Li and metal which

is not alloyed, and may be formed from an alloy of Li, metal which is not alloyed, Li, and metal to alloy. Li contained in this alloy and metal to alloy may be the same metal as Li which constitutes an active material layer, and metal to alloy, and may be different metal. For example, when an active material layer is formed from Sn, an alloy in a surface coated layer may be an alloy of Sn, and may be Li of others, such as germanium, and an alloy of metal to alloy.

[0012]Li of a surface coated layer and metal which is not alloyed may be the same metal as Li of a collector layer, and metal which is not alloyed, and may be different metal. For example, when a collector layer consists of Cu(s), a surface coated layer may be Cu and may be Li of others, such as Fe, and metal which is not alloyed.

[0013]In this invention, an active material layer is provided on a collector layer. A method of forming an active material layer is mentioned by depositing Li and metal to alloy on a substrate used as a collector layer as one of the methods which provides an active material layer on a collector layer. For example, an active material layer which consists of Sn can be formed by depositing Sn on Cu boards, such as copper foil used as a collector layer. A method of forming a collector layer is mentioned by depositing Li and metal which is not alloyed on a substrate used as an active material layer as other methods. For example, a collector layer which consists of Cu(s) can be formed by depositing Cu on Sn boards, such as tinfoil used as an active material layer. As a method of forming an active material layer and a collector layer, the plating method, sputtering process, vacuum deposition, etc. are mentioned. A CVD method and a vacuum deposition method are mentioned as vacuum deposition. As a plating method, the electrolysis plating method and a nonelectrolytic plating method are mentioned.

[0014]In this invention, a compound phase which an ingredient of a surface coated layer and an ingredient of an active material layer mixed to an interface of a surface coated layer and an active material layer may be formed. Such a compound phase can be formed by heat-treating, for example, after forming a surface coated layer on an active material layer. In this compound phase, an ingredient of a surface coated layer and an ingredient of an active material layer may form a solid solution and an intermetallic compound. A compound phase may be crystallinity and may be amorphous.

[0015]As a temperature of heat treatment for forming the above-mentioned compound phase, it is preferred that it is 50% - about 105% of temperature of the melting point of the lower one among the melting point of metal of a surface coated layer or an alloy and metal of an active material layer, or the melting point of an alloy. Since the melting point of Cu is 1085 ** and the melting point of Sn is 232 ** when using a Sn layer as an active material layer, using a Cu layer as a surface coated layer, it is preferred to heat-treat at 50% - 105% of temperature of 232 ** which is the melting point of the lower one, i.e., temperature within the limits of 116-243 **. In order to form a compound phase more effectively, it is preferred to heat-treat at temperature within the limits of further 160-240 **. In the case of such heat treatment, a compound phase

which an ingredient of an active material layer and an ingredient of a collector layer mixed may be formed in an interface of an active material layer and a collector layer.

[0016]In this invention, it is desirable still more preferred that it is 0.2 micrometer or less, and thickness of a surface coated layer is 0.1 micrometer or less. If thickness of a surface coated layer becomes thick too much, a reaction of an active material layer and Li in an electrolysis solution is checked, and charge-and-discharge capacity may fall. As for thickness of a surface coated layer, it is preferred that it is 0.01 micrometers or more. Therefore, as for thickness of a surface coated layer, it is preferred that it is about 0.01-0.2 micrometer. If thickness of a surface coated layer becomes thin too much, an effect of inhibiting a reaction of an active material layer and an electrolysis solution may not fully be acquired.

[0017]In this invention, when forming an active material layer by making Li and metal to alloy deposit on a substrate used as a collector layer, it is preferred that unevenness is formed in a substrate face. By forming unevenness in a substrate face, the adhesion of a substrate and an active material layer can improve and omission of an active material layer accompanying a charge-and-discharge reaction can be controlled. As for surface roughness Ra of a substrate, it is preferred that it is about 0.01-2 micrometers. Surface roughness Ra is provided in Japanese Industrial Standard (JIS B 0601-1994), for example, can be measured with a surface roughness meter. As big copper foil of surface roughness Ra, electrolytic copper foil is known and it is preferred to use such electrolytic copper foil as a substrate. As for thickness of a substrate, if per volume and an energy density per weight are taken into consideration, it is preferred that it is about 50 micrometers or less.

[0018]This invention is characterized by a lithium secondary battery comprising the following.

A negative electrode which consists of an electrode for lithium secondary batteries of above-mentioned this invention.

Anode.

Nonaqueous electrolyte.

A solvent of an electrolyte used for a lithium secondary battery of this invention, Although not limited in particular, cyclic carbonate, such as ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate, A mixed solvent with chain carbonate, such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, is illustrated. A mixed solvent of said cyclic carbonate and ether system solvents, such as 1,2-dimethoxyethane and 1,2-diethoxyethane, is also illustrated. As an electrolytic solute, LiPF_6 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$, Those mixtures, such as $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ and $\text{LiC}(\text{C}_2\text{F}_5\text{SO}_2)_3$, are illustrated. Furthermore, inorganic solid electrolytes, such as a gel polymer electrolyte with which polymer electrolytes, such as polyethylene oxide and polyacrylonitrile, were impregnated in an electrolysis solution, LiI , Li_3N , are illustrated as an electrolyte. An

electrolyte of a lithium secondary battery of this invention can be used without restrictions, unless Li compound as a solvent which makes ion conductivity reveal, and a solvent which dissolves and holds this decompose on voltage at the time of charge of a cell, discharge, or preservation.

[0019]As positive active material of a lithium secondary battery of this invention, LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , Lithium containing transition metal oxides, such as LiMnO_2 , $\text{LiCo}_{0.5}\text{nickel}_{0.5}\text{O}_2$, and $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$, and a metallic oxide which does not contain lithium, such as MnO_2 , are illustrated. In addition, if it is a substance electrochemically inserted and desorbed from lithium, it can use without restriction.

[0020]

[Embodiment of the Invention]Although this invention is hereafter explained still in detail based on an example, in the range which is not limited to the following examples at all and does not change the gist, it changes suitably and this invention can be carried out.

[0021](Experiment 1)

[Production of an electrode] On 18-micrometer-thick electrolytic copper foil (surface roughness $R_a = 0.188$ micrometer), the 2-micrometer-thick tin thin film was formed by the electrolysis plating method. As a plating bath, the thing of the presentation shown in Table 1 was used, using tin as the anode.

[0022]

[Table 1]

物質名	濃度
硫酸第一錫	$40 \text{ g} \cdot \text{dm}^{-3}$
硫酸 (98%)	$150 \text{ g} \cdot \text{dm}^{-3}$
ホルマリン	$5 \text{ cm}^3 \cdot \text{dm}^{-3}$
添加剤(上村工業製)	$40 \text{ cm}^3 \cdot \text{dm}^{-3}$

[0023]The tin thin film which is an active material layer was formed on the electrolytic copper foil which is a collector layer as mentioned above. Next, the 0.02-micrometer-thick Cu layer was formed by the electrolysis plating method on this tin thin film. As a plating bath, the thing of the presentation shown in Table 2 was used, using copper as the anode.

[0024]

[Table 2]

物質名	濃度
シアン化銅	$20 \text{ g} \cdot \text{dm}^{-3}$
シアン化ナトリウム	$30 \text{ g} \cdot \text{dm}^{-3}$

[0025]On the tin thin film which is an active material layer as mentioned above, the Cu layer which is a surface coated layer was formed. Thus, the obtained electrode was used as this invention electrode a1. Like the above, after forming a tin thin film on

electrolytic copper foil, 0.02-micrometer-thick Sn-Cu alloy layer was formed by the electrolysis plating method on the tin thin film. As a plating bath, the thing of the presentation shown in Table 3 was used, using the separation anode of copper and tin as the anode. The thickness of the thin film formed with plating and a layer is the value calculated from the current and time at the time of plating. It is thought that an above-mentioned Cu layer and Sn-Cu alloy layer have not covered the tin thin film top uniformly, and have distributed for it and covered it to island shape since the thickness is dramatically thin.

[0026]

[Table 3]

物質名	濃度
シアン化銅	11 g · dm ⁻³
スズ酸ナトリウム(3水塩)	90 g · dm ⁻³
シアン化ナトリウム	27 g · dm ⁻³
水酸化ナトリウム	16 g · dm ⁻³

[0027]On the tin thin film which is an active material layer as mentioned above, Sn-Cu alloy layer which is a surface coated layer was formed. Thus, the obtained electrode was used as this invention electrode a2. What formed the tin thin film on electrolytic copper foil like the above as comparison was produced, and this was made into the reference electrode b1. Therefore, in the reference electrode b1, the surface coated layer is not formed on a copper thin film.

[0028][Production of an electrolysis solution] 1 mol/l. of LiPF₆ was dissolved in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate, and the electrolysis solution was produced.

[0029][Production of a beaker cell] The beaker cell as shown in drawing 2 was produced using as a working pole what cut off each above-mentioned electrode in size of 2 cm x 2 cm. As shown in drawing 2, the beaker cell is constituted by immersing the counter electrode 3, the working pole 4, and the reference pole 5 into the electrolysis solution into which it was put in the container 1. The lithium metal was used as the counter electrode 3 and the reference pole 5, using the above-mentioned electrolysis solution as the electrolysis solution 2.

[0030][Measurement of a cycle characteristic] Perform the beaker cell produced as mentioned above at 25 **, and constant current charge is performed to 0V (vs.Li/Li⁺) at 0.2 mA, respectively, Constant current discharge was performed to 2V (vs.Li/Li⁺) at 0.2 mA after that, charge and discharge were performed up to 10 cycle by having made this into one cycle, and the capacity maintenance rate defined as the following formulas was searched for. A result is shown in Table 4. Here, reduction of a working pole is considered as charge and oxidation of the working pole is considered as discharge.

[0031]Capacity maintenance rate (%) =(service capacity of service capacity / 1 cycle

eye of 10 cycle eye) x100 [0032]

[Table 4]

電 極	表面被覆層の 種類	表面被覆層の 厚み (μm)	200℃24時間 熱処理の有無	容量維持率 (%)
本発明電極 a1	Cu	0.02	無	41
本発明電極 a2	Sn-Cu	0.02	無	50
比較電極 b1	—	0	無	17

[0033]Compared with the reference electrode b1 in which this invention electrodes a1 and a2 in which the surface coated layer was formed on the active material layer do not form the surface coated layer on an active material layer, the capacity maintenance rate is high so that clearly from the result shown in Table 4. This is considered to be because for the reaction of the active material layer surface and an electrolysis solution to have been inhibited when a surface coated layer exists on the surface of an active material layer.

[0034](Experiment 2) The 2-micrometer-thick tin thin film was formed by the electrolysis plating method like the experiment 1 on 18-micrometer-thick electrolytic copper foil (surface roughness Ra = 0.188 micrometer). Next, using the plating bath of the presentation shown in Table 2 like the experiment 1, the Cu layer as 0.05 micrometer in thickness and a 0.2-micrometer surface coated layer was formed on the tin thin film, and each was heat-treated at 200 ** after that for 24 hours. It was checked that the compound phase is formed in the interface of a Cu layer and a tin thin film by heat treatment, respectively. What formed this invention electrode c1 and a 0.2-micrometer Cu layer for the thing in which the 0.05-micrometer-thick Cu layer was formed was used as this invention electrode c2.

[0035]As comparison, the reference electrode b1 was heat-treated at 200 ** for 24 hours, and it was considered as the reference electrode d1. The beaker cell was produced like the above-mentioned experiment 1, the charge and discharge test was done, and the capacity maintenance rate was searched for. A result is shown in Table 5.

[0036]

[Table 5]

電 極	表面被覆層の 種類	表面被覆層の 厚み (μm)	200℃24時間 熱処理の有無	容量維持率 (%)
本発明電極 c1	Cu	0.05	有	88
本発明電極 c2	Cu	0.2	有	87
比較電極 d1	—	0	有	80

[0037]Compared with the reference electrode d1, this invention electrode c1 and c2 in_which the surface coated layer was formed show the high capacity maintenance rate so that clearly from the result shown in Table 5. This is considered to be because for the reaction of the active material layer surface and an electrolysis solution to have been inhibited by forming a surface coated layer.

[0038]Drawing 1 shows the charging curve of the two-cycle eye of this invention electrode c1 and the reference electrode d1. A horizontal axis shows a charging rate and the vertical axis shows the potential for lithium. The profile considered to be a reaction with an electrolysis solution in the potential 1.1V for lithium neighborhood which was not seen by 1 cycle eye with the reference electrode d1 was accepted, and charge and discharge efficiency was as low as 81%. On the other hand, in this invention electrode c1, such a profile was not accepted but its charge and discharge efficiency was also as high as 99%. Therefore, when a surface coated layer exists on the surface of an active material layer, by this invention electrode c1, it is thought that the reaction of the active material layer surface and an electrolysis solution is inhibited, and it is thought by it that good charge and discharge efficiency is acquired by this control, and good charge-and-discharge cycle life property is acquired.

[0039]

[Effect of the Invention]According to this invention, service capacity is large and it can be considered as the electrode for lithium secondary batteries excellent in the charge-discharge cycle characteristic.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]The figure showing the charging curve of the two-cycle eye of this invention electrode according to this invention.

[Drawing 2]The typical sectional view showing the beaker cell produced in the example of this invention.

[Description of Notations]

- 1 -- Container
- 2 -- Electrolysis solution
- 3 -- Counter electrode
- 4 -- Working pole
- 5 -- Reference pole